MODELING AND SIMULATION OF PYROLYSIS PROCESS FOR A BEECH WOOD MATERIAL

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Abstract

Modeling and simulation of beech wood was carried out using Aspen Plus simulation commercial package. The model was created based on pyrolysis product yield, proximate and ultimate analysis of the wood species. In the model development, RYield was used to represent pyrolysis reactor as a non- stoichiometric type that decomposes the wood into categories of conventional compounds. The model was simulated to give the components compositions in both gaseous and liquid products. The simulation was first conducted at a temperature of 450°C, for range of feed particle sizes from 1.6-2.0 mm, using atmospheric pressure. Five different runs were carried out by varying their temperatures and particle size. The investigation revealed the effect of pyrolysis temperature and wood particle size on compositions of liquid and gaseous products. The results showed that production of methanol increases with temperature but decreases at temperatures beyond 550°C. Carbon dioxide yield decreases with increase in temperature while that of carbon monoxide and methane get higher as temperature increases.

Keywords: Aspen Plus, Beech Wood, Composition, Pyrolysis, Ryield

1. Introduction

Pyrolysis is a process which thermally breaks down higher molecular carbonaceous compound to produce lower molecular compounds in an oxygen-devoid environment at considerably high temperature. High temperature is needed for the disintegration of the feedstock molecules into smaller molecular compounds. The products of pyrolysis are condensable gases known as bio-oil or pyrolytic oil, bio-char and non-condensable gases (Mohammed *et al.,* 2015). A carbonaceous material disintegrates into vapour and bio-char on application of heat (Gulzad, 2011). The vapour consists of condensable gases that transform into liquid (bio-oil) after condensation while the non-condensables are collected or vented as gases. High generation of biomass and its potential in production of bio-oil makes it a promising source of renewable energy (Hossain *et. al.*, 2014).

Wood is an important forest product and residue. Forest serves as renewable source of wood and residue due to its ability to replenish itself. Wood is used as raw solid fuel in form of fire wood and feedstock for thermochemical processing into various kinds of products.

Modeling and simulation of biomass pyrolysis process provide a basis for its understanding and analysis as well as large scale development and optimization. In modeling biomass pyrolysis, better understanding of the physical changes, heat transfer, reactions involved and interaction with the reactor environment are considered (Lam *et al*., 2012). Modeling and simulation of pyrolysis process is gaining attention because of the growing interest in pyrolysis of forest residues and agricultural waste for the production of liquid and gaseous chemicals. This gives, for example, the pyrolysis process of biomass that provides the basis for understanding, optimizing, and large scale development of the systems. In modeling the biomass pyrolysis, the physical changes, heat transfer, reaction and its interactions with the reactor environment are typically considered.

Blasi (2006) review covered both physical and chemical processes involved in pyrolysis, Gentile *et al.* (2015) developed a model based on Computational Fluid Dynamics (CFD) approach. Gentile *et al*. (2015) described the role of reaction kinetics and transport phenomena in pyrolysis of biomass at particle scale. Chew *et al*. (2011) modelled the pyrolysis of Nyatoh and Kapur wood under isothermal conditions in air based on weight loss history. The empirical model was built with data collected on different species of hardwood at low temperatures. They showed that the reaction order that corresponds to the rates, the estimates of heating duration to reach different degrees of degradation as a function of temperature were observed. They also compare the chemisorption

characteristics and reactivity of aerobic wood char and their propensity to self-ignition. Homma *et al.* (2014) presented models that described pyrolysis reactions based on the number of moles of product species that were generated. Kazakova *et al.* (2015) built biomass pyrolysis model based on multistep devolatilization of the three main biomass components (cellulose, hemicelluloses, and lignin) which led to determination of the liquid, solid and gaseous phases at any point in the process.

No literature to the best of my knowledge reported a model set to give estimates of actual compositions of products obtainable from pyrolysis of beech wood. The objectives of this work are to model and simulate pyrolysis process of beech wood in order to estimate compositions of individual compounds in both liquid and gaseous products and to study the effect of pyrolysis temperature and wood particle size on the products compositions.

The study will give an idea of compositions of various products expected from pyrolysis of the wood specie, which will help an interested researcher in knowing the expected products and their compositions at various pyrolysis temperatures.
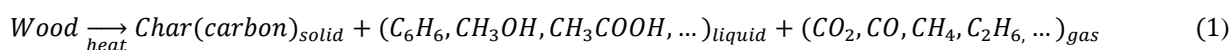
2.   Materials and methods

Beech wood (*Fagus sylvatica* L.) is a hard wood specie abundant in Europe, extending from southern Norway to northern Spain and from the south of England to the Black Sea found mainly in public forests. The composition of Beech wood obtained from proximate and ultimate analysis, (Table 1) was used in this work. The components of the product stream are substances on the right hand side of Equation 1. The development of the process model was carried out using Aspen Plus Software, Version 8.4. Aspen Plus has no in-built pyrolysis reactor, hence the reactor was modelled as RYield, which is a non-stoichiometric reactor that was based on known yield distribution that decomposed the wood into solid, liquid and gas containing different compounds as in equation 1.

Table 1: Beech Wood Composition

Ultimate analysis	(%wt)	Proximate analysis(% wt)	
Carbon	49.2	Volatile matter	85.3
Hydrogen	6	Fixed carbon	14.3
Oxygen	44.1	Moisture	0
Nitrogen	0.5	Ash	0.4
Sulphur	0.02		

Source: Rabacal *et al.* (2014).

Wood was modelled as solid made up of free elements and compounds of given compositions presented in Table 1. The wood get decomposed upon heating in an oxygen deficient environment to yield the products of equation 1. Char was modelled as solid containing mainly carbon. The liquid product was modelled by defining the compounds (C_6H_6, CH_3OH, CH_3COOH etc.) from the software's data base. The gaseous products were also modelled in the same manner with the liquid.

$$Wood \xrightarrow[heat]{} Char(carbon)_{solid} + (C_6H_6, CH_3OH, CH_3COOH, \dots)_{liquid} + (CO_2, CO, CH_4, C_2H_{6,} \dots)_{gas} \qquad (1)$$

Model Assumptions
➢   Steady state operation was considered
➢   The temperature in each block was considered uniform with negligible heat losses
➢   The wood chips are of variable particle sizes and spherical in shape
➢   The char is virtually made up of carbon
➢   The model was based on law of conservation of matter as depicted in equation 2

$$M_{in} + M_{gen} = M_{out} + M_{acc} + M_{con} \tag{2}$$

In pyrolysis no mass is consumed or generated, hence equation 2 reduced to Eqn. 3

$$M_{in} = M_{out} + M_{acc} \tag{3}$$

where: M_{in} represents the amount of wood fed into pyrolysis reactor, M_{out} represents the volatiles (liquid and gas) and M_{acc} stands for the char.

The model represents the decomposition of beech wood into various products as depicted in Equation 1. Development of the process model was carried out using Aspen Plus Software, Version 8.4. Beech wood does not exist in the software's library, but was created hypothetically using its proximate and ultimate analysis that is presented in Table 1. But every other component used the conventional compounds from the software's library. In choosing the property package, ideal equation of state was adopted due to high temperatures involved in the process. RYield was used to represents the pyrolysis reactor (PYRO-RE) which allows the decomposition of non-conventional solid into conventional material. RYield is a non-stoichiometric reactor based on known yield distribution, hence suitable for the representation of pyrolysis which involves non-stoichiometric reactions. Studies show that pyrolysis of hard wood normally starts from 400°C, hence Table 2 presents the operating parameters of the heart of the process, which was pyrolysis reactor (PYRO-RE). Pyrolysis product separator was represented by CYCLONE to separate the pyrolysis product from the reactor into volatiles and char. A cooling system (cooler) was used to represents CONDENSER which quenches the volatiles into liquid (bio-oil) and non-condensable gases. The complete pyrolysis model built in the simulation environment is depicted in Figure 1.

Table 2: PYRO-RE Inputs Operating Conditions

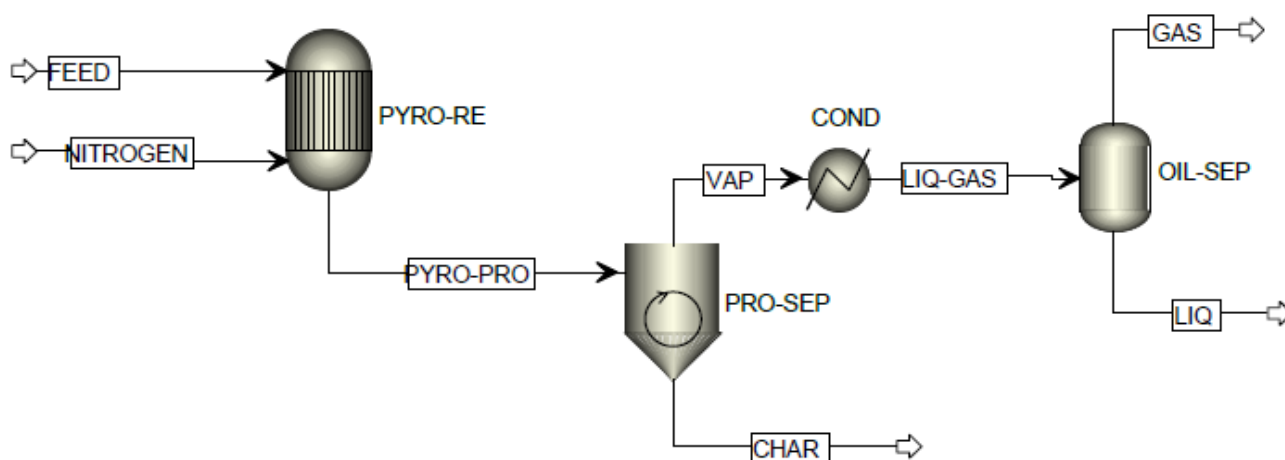|	
Feed flow rate	10 kg/hr.
Feed particle size	1.6-2.0 mm
Pyrolysis temperature	450 °C
Pyrolysis Pressure	1 atm
Nitrogen gas flow rate	0.2 kg/min

Figure1: The model flow chart showing the beech wood pyrolysis process

3.   Results and Discussion
3.1   Model Validation
The model (Figure 1) was rerun 5 times at varying temperatures to compute the products compositions. The results of the simulation at 400°C were compared with experimental data presented by Bajus (2010) at the same temperature as shown in Table 3.The standard deviation was found to be 0.47 which shows closeness of the model's results to that of the experiment.

Table 3: Simulated products composition compared with experimental results of Bajus (2010)

Components	Compositions (%wt)		error
	400 °C (Modeled)	400 °C (Bajus, 2010)	
CO_2	50.67	52.80	2.13
CO	34.88	34.70	0.18
Methane	5.21	6.20	0.99
Ethane	1.37	1.50	0.13
Ethylene	1.21	1.00	0.21
Propane	0.36	0.50	0.14
Propene	1.37	1.10	0.27
Methylpropane	0.03	0.02	0.01
Butane	0.08	0.09	0.01
trans-2-Butene	0.12	0.10	0.02
1-Butene	0.24	0.20	0.04
Methylpropene	0.12	0.20	0.08
cis-2-Butane	0.12	0.10	0.02
1, 3-Butadiene	0.10	0.09	0.01
trans-2-Pentene	0.02	0.03	0.01
1, 3-Pentadiene	0.04	0.04	0.00
2-Methyl-2-butene	0.05	0.04	0.01
c5-hydrocarbons	0.04	0.05	0.01
Pentane	0.02	0.03	0.01
2-Methyl-1-butene	0.05	0.04	0.01
1-Hexan	0.18	0.20	0.02
Benzene	0.46	0.50	0.04

3.2 Effect of pyrolysis temperature on products compositions
Temperature is one of the key factors affecting product distribution in pyrolysis of biomass. To study the effect of pyrolysis temperature, simulations were performed by varying temperatures between 400 and 600°C because pyrolysis of hard wood begins from temperature as high as 400°C (Homma *et al*., 2014). The distribution of components by percentage weight in the gaseous stream at varied temperatures from 400 to 600°C was depicted in Figure 2. The notable species of gases from the Beech wood pyrolysis are carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH4). The result shows that CO_2 decreased with increase in temperature and the yield of CO decreased slightly as temperature increased from 400-450 °C. This might be as the result of decomposition of CO_2 to form more CO just as reported by Prins and Jensen (2006).These led to the depletion of the CO_2 as it was formed. The variation in CO_2 and CO composition with temperature in this model is also in agreement with that presented by Paviet *et al*. (2009) in their study of temperature effect on biomass thermochemical treatment. Methane which was the third most abundant component in the gas stream increased linearly with temperature, and this is interesting because of its usefulness as source of fuel. Ethane and ethylene were also noticed to increase as the

pyrolysis temperature gets higher. Temperature change did not provide significant effect on propene production.

Bio-oil which formed the liquid stream contained many species. Most of the higher molecular species' compositions decreased with increase in temperature due to their instability at higher temperatures which subsequently led to further breakdown into lighter gaseous components. Figure 3 shows the influence of temperature on some major liquid products.
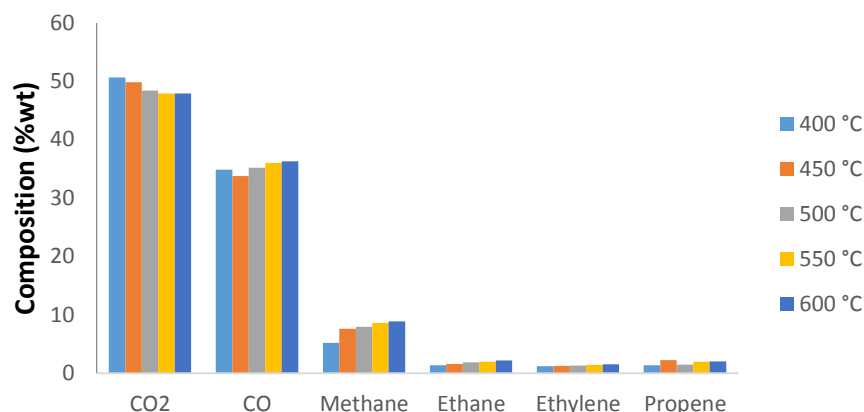

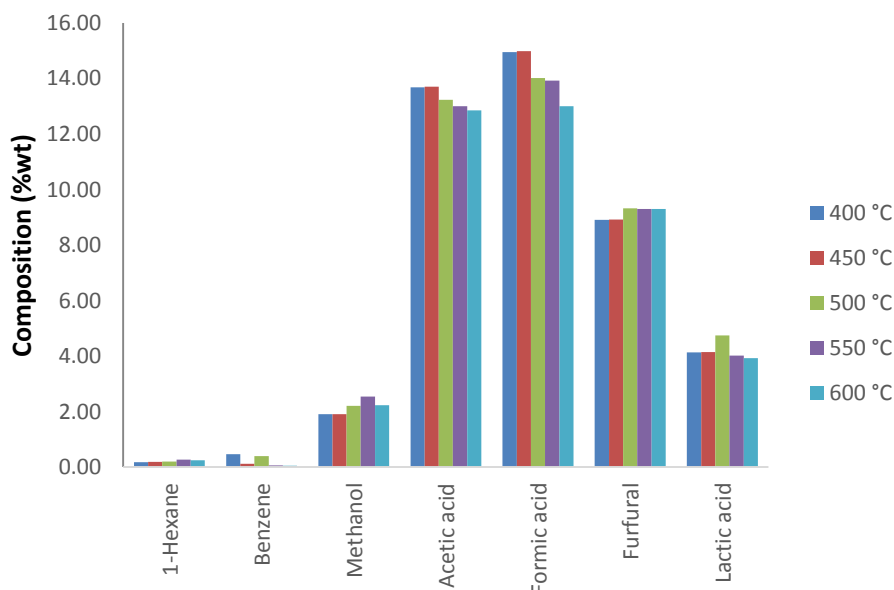Figure 2: Effects of temperature on gaseous products from beech wood pyrolysis

Figure 3: Plot of bio-oil compositions at different temperatures

Acetic acid composition was not affected by temperature increase from 400 to 450 ^{o}C, the effect becomes more pronounced when the temperature reached 500°C. Formic acid followed the same trend but sharp decrease in composition with temperature increased from 550°C to 600°C was recorded as compared to that of acetic acid. Temperature increase shows significant reduction in the gross compositions of acetic, formic and lactic acids respectively. This might have resulted from decarboxylation of acids groups present in wood to form CO_2 at high temperatures. This led to increase in CO due to reaction of CO_2, steam and porous char. Furfural was the third most considerable components after acetic acid, formic acid and lactic acid in terms of composition. Temperature increase was accompanied by slight increase in furfural formation up till 500°C before

it started decreasing. High composition of the furfural was achieved at 500°C, beyond which its production was not favoured. Further temperature increase did not favour the production of the product.

Temperature shows no significant change in the composition of methanol as with benzene which was in trace amount. 1-Hexene composition was not affected much with temperature change. Production of methanol composition increases with temperature increase up to 550°C. At higher temperature of 550°C, methanol composition dropped. Benzene composition decreases with increasing pyrolysis temperatures.

The decrease in the overall bio-oil contents at higher temperatures may be emanated from secondary reaction which cracked some of the liquid components into non-condensable gases.

3.3 Effect of particle size on gaseous and liquid compositions

Wood particle size distribution also plays a significant role in both product and components distribution of pyrolysis process. Plot of the compositions of most significant gases and liquid products at varying feed particle size range were depicted in Figure 4 and Figure 5 respectively.
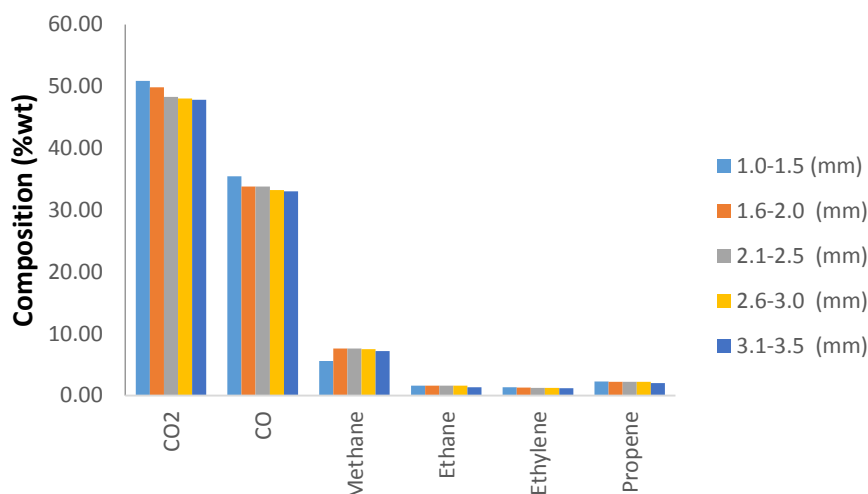

Figure 4: Effect of feed particle sizes on gaseous products composition
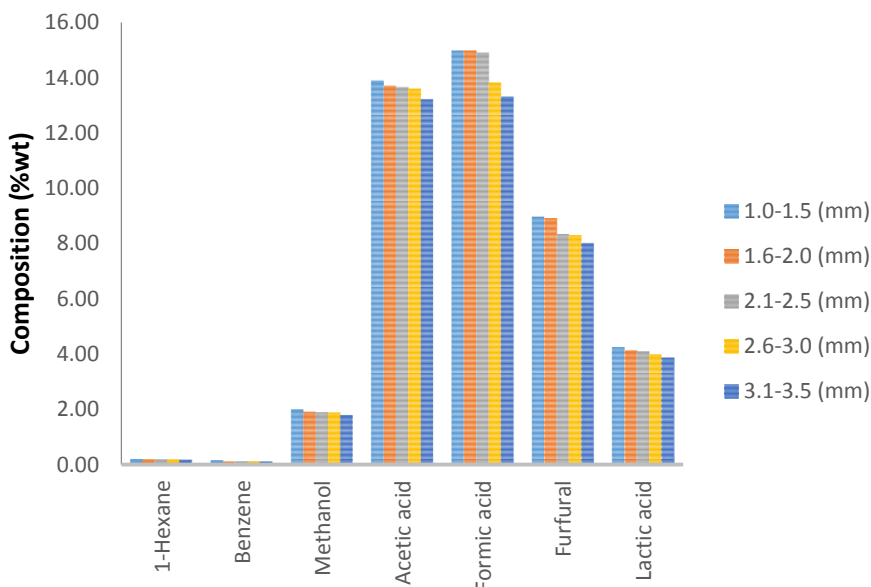

Figure 5: Effect of feed particle size on liquid components distribution

The results show a general reduction in the compositions of the gases. This may be explained in terms of heat transfer resistance offered by larger sizes of the wood which prevents full decomposition of feed into volatiles. The bio-oil components also diminished as the particle sizes get larger.

4.   Conclusion

A model of pyrolysis process of Beech wood was created and simulated. Effects of pyrolysis conditions on products compositions were in. It was found that temperature has significant impact in determining products compositions. The model is credible enough to estimate the composition of different compounds obtainable from pyrolysis of beech wood. Carbon dioxide and carbon monoxide formed the highest part of the gaseous product followed by methane, ethane and ethylene. Temperature range of 450 to $550^{o}C$ suggested good yield of methane and ethane. The liquid fuel yields were also favoured around this temperature range but the fuel tends to be acidic due to higher concentration of formic, acetic and lactic acids. However, at higher temperatures of 500 to $600^{o}C$ the acidic groups undergo secondary reactions to form more CO_2 which broke into CO by secondary reaction as well. Production of more CO at higher temperatures suppressed higher yield of CO_2 from the breakdown of the acidic groups. It was established that methanol, a very useful compound could be obtained at appreciable yield at a pyrolysis temperature of $550^{o}C$.

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